

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

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| Applicant's or agent's file reference P100899WO | FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416) | |
| International application No. PCT/GB 03/04665 | International filing date (day/month/year) 30.10.2003 | Priority date (day/month/year) 04.11.2002 |
| International Patent Classification (IPC) or both national classification and IPC C22C30/00 | | |
| Applicant DONCASTERS LIMITED et al. | | |



1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of 11 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☒ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

| | |
|---|--|
| Date of submission of the demand 01.06.2004 | Date of completion of this report 10.03.2005 |
| Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 | Authorized Officer Catana, C Telephone No. +49 89 2399-7369  |

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/GB 03/04665**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-25 as originally filed

Claims, Numbers

1-41 received on 20.10.2004 with letter of 20.10.2004

Drawings, Sheets

1/8-8/8 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☒ the claims, Nos.: 42-52
- ☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB 03/04665

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:
- ☐ the entire international application,
 - ☒ claims Nos. 20,36, 38-40
- because:
- ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (specify):
 - ☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):
 - ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
 - ☒ no international search report has been established for the said claims Nos. 21, 22,44,46,47,50 (as originally filed)
2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:
- ☐ the written form has not been furnished or does not comply with the Standard.
 - ☐ the computer readable form has not been furnished or does not comply with the Standard.

IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees, the applicant has:
- ☐ restricted the claims.
 - ☐ paid additional fees.
 - ☐ paid additional fees under protest.
 - ☒ neither restricted nor paid additional fees.
2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/GB 03/04665**

☐ complied with.

☐ not complied with for the following reasons:

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

☐ all parts.

☒ the parts relating to claims Nos. 1-19,21-35, 37, 41 .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

| | | |
|-------------------------------|-------------|------------------|
| Novelty (N) | Yes: Claims | |
| | No: Claims | 1-19,21-35,37,41 |
| Inventive step (IS) | Yes: Claims | |
| | No: Claims | 1-19,21-35,37,41 |
| Industrial applicability (IA) | Yes: Claims | 1-19,21-35,37,41 |
| | No: Claims | |

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB 03/04665

1. The subject-matter of claim 1 is directed to an oxide dispersion strengthened Ni-Cr-Fe alloy as defined in claim 1 (C 0.01-0.7, Si 0.1-3, 15-90 Ni, 5-40 Cr, 0.01-4.5 Hf, balance iron and imp.), having Hf as fine oxide particles and at least one carbide forming element more stable than Cr: Nb, Ti, W, Ta and Zr.

2. Reference is made to the following documents:

D1: EP-A-0050408

D2: US 6409847

D3: JP-A-05001355

D4: EP-A-0391381

D5: US 5851318

3. Novelty

3.1 D1 describes a Ni-Cr-Fe alloy. The composition of alloy of example C falls within the ranges as defined in claim 1 (see page 5, line 4). Alloy C contains Ti (a carbide forming element) and also 0.52 wt% Hf.

The method of producing the alloy according to the present invention is defined in claim 22. Since the method of D1 as described at page 4, line 1-12, includes the step of adding Hf before pouring as defined in claim 26, it would inevitably result in the same alloy, i.e. having at least part of Hf as oxide particles.

The subject-matter of independent claim 1 and 22 lacks novelty over the disclosure of D1 (Art. 33.2 PCT).

Following the same approach, D1 is considered as anticipating the subject-matter of claims:

2, 4, 6, 8, 10, 15, 16, 17, 21, 41 in respect of alloy;

23,29 in respect of method;

37 in respect of the tube (pipe).

3.2 In addition, the following prior art is also considered to be novelty destroying for the cited claims:

21, 41 in respect of alloy in D2 (table 1), D3 (table 1, ex. 1-4), D4 (ex. 17, table 1), D5 (table 1, ex. A-F);

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB 03/04665

37 in respect of the tube (pipe) in D2 (claim 6), D3 (par. 18; abstract), D4 (page 5, line 32-34), D5 (col. 5, line 16-24).

The use of a rotational moulding to produce a tube is described i.e. in D2 (par. 16), D3 (par. 18), D4 (page 5, line 32-34).

- 3.3 The subject-matter of remaining dependent claims does not appear to add any inventive features to independent claim 1 and/or 22.
4. The amendments made on 20.10.2004 to claims 20, 36, 38, 39, 40 are not allowable since they relate to unsearched matter either lacking unity (Rule 13.1 PCT) or undefined and obscure (Rule 6.2(a) PCT) as detailed in the International Search Report; the subject-matter of these claims is therefore not examined; the subject-matter of claims 37, 41 which refers back to any of above-mentioned claims is also not to be examined. The rest of the amendments is considered to comply with Art. 19 PCT.

CLAIMS

1. An oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

5

Carbon 0.01 - 0.7%

Silicon 0.1 - 3.0%

Manganese 0 - 2.5%

Nickel 15 - 90%

10 Chromium 5 - 40%

Molybdenum 0 - 3.0%

Niobium 0 - 2.0%

Tantalum 0 - 2.0%

Titanium 0 - 2.0%

15 Zirconium 0 - 2.0%

Cobalt 0 - 2.0%

Tungsten 0 - 4.0%

Hafnium 0.01 - 4.5%

Aluminium 0 - 15%

20 Nitrogen 0.001 - 0.5%

Oxygen 0.001 - 0.7%

balance iron and incidental impurities,

with the proviso, that at least one carbide forming
25 element whose carbide is more stable than chromium
carbide selected from niobium, titanium, tungsten,
tantalum and zirconium is present and that at least part
of the hafnium is present as finely divided oxide
particles.

30

2. An oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

Carbon 0.01 to 0.5%

35 Silicon 0.01 to 2.5%

27

| | | |
|----|------------|---------------|
| | Manganese | 0 to 2.5% |
| | Nickel | 15 to 50% |
| | Chromium | 20 to 40% |
| | Molybdenum | 0 to 1.0% |
| 5 | Niobium | 0 to 1.7% |
| | Titanium | 0 to 0.5% |
| | Zirconium | 0 to 0.5% |
| | Cobalt | 0 to 2.0% |
| | Tungsten | 0 to 1.0% |
| 10 | Hafnium | 0.01 to 4.5%, |

balance iron and incidental impurities,

15 with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

3. An alloy according to claim 1 having the following composition, by weight:

20

| | | |
|----|---|--------------|
| | Carbon | 0.3 to 0.7% |
| | Silicon | 0.1 to 2.5% |
| | Manganese | 2.5% max. |
| | Nickel | 30 to 40% |
| 25 | Chromium | 20 to 30% |
| | Molybdenum | 3.0% max. |
| | Niobium | 2.0% max. |
| | Hafnium | 0.01 to 4.5% |
| | Titanium | 0.5% max. |
| 30 | Zirconium | 0.5% max. |
| | Cobalt | 2.0% max. |
| | Tungsten | 1.0% max. |
| | Nitrogen | 0.001 - 0.5% |
| | Oxygen | 0.001 - 0.7% |
| 35 | Balance iron and incidental impurities. | |

4. An alloy according to claim 1 having the following composition, by weight:

| | | |
|----|---|--------------|
| | Carbon | 0.03 to 0.2% |
| 5 | Silicon | 0.1 to 0.25% |
| | Manganese | 2.5% max. |
| | Nickel | 30 to 40% |
| | Chromium | 20 to 30% |
| | Molybdenum | 3.0% max. |
| 10 | Niobium | 1.7% max. |
| | Hafnium | 0.01 to 4.5% |
| | Titanium | 0.5% max. |
| | Zirconium | 0.5% max. |
| | Cobalt | 2.05% max. |
| 15 | Tungsten | 1.0% max. |
| | Aluminium | 0 - 15.0% |
| | Nitrogen | 0.001 - 0.5% |
| | Oxygen | 0.001 - 0.7% |
| | balance iron and incidental impurities. | |

20

5. An alloy according to claim 1 having the following composition, by weight:

| | | |
|----|------------|--------------|
| | Carbon | 0.3 to 0.7% |
| 25 | Silicon | 0.01 to 2.5% |
| | Manganese | 2.5% max. |
| | Nickel | 40 to 60% |
| | Chromium | 30 to 40% |
| | Molybdenum | 3.0% max. |
| 30 | Niobium | 2.0% max. |
| | Hafnium | 0.01 to 4.5% |
| | Titanium | 1.0% max. |
| | Zirconium | 1.0% max. |
| | Cobalt | 2.0% max. |
| 35 | Tungsten | 1.0% max., |

29

Aluminium 0 - 15.0%
Nitrogen 0.001 - 0.5%
Oxygen 0.001 - 0.7%
balance iron and incidental impurities.

5

6. An alloy according to claim 1 having the following composition, by weight:

| | | |
|----|---|--------------|
| | Carbon | 0.03 to 0.2% |
| 10 | Silicon | 0.1 to 2.5% |
| | Manganese | 2.5% max. |
| | Nickel | 40 to 50% |
| | Chromium | 30 to 40% |
| | Molybdenum | 3.0% max. |
| 15 | Niobium | 2.0% max. |
| | Hafnium | 0.01 to 4.5% |
| | Titanium | 0.5% max. |
| | Zirconium | 0.5% max. |
| | Cobalt | 2.0% max. |
| 20 | Tungsten | 1.0% max., |
| | Aluminium | 0 - 15.0% |
| | Nitrogen | 0.001 - 0.5% |
| | Oxygen | 0.001 - 0.7% |
| | balance iron and incidental impurities. | |

25

7. An alloy according to claim 1 having the following composition, by weight:

| | | |
|----|------------|--------------|
| | Carbon | 0.3 to 0.7% |
| 30 | Silicon | 0.01 to 2.5% |
| | Manganese | 2.5% max. |
| | Nickel | 19 to 22% |
| | Chromium | 24 to 27% |
| | Molybdenum | 3.0% max. |
| 35 | Niobium | 2.0% max |

30

Hafnium 0.01 to 4.5%
Cobalt 2.0% max.
Tungsten 1.0% max.,
Aluminium 0 - 15.0%
5 Nitrogen 0.001 - 0.5%
Oxygen 0.001 - 0.7%
balance iron and incidental impurities.

8. An alloy according to claim 1 having the following
10 composition, by weight:

Carbon 0.03 to 0.2%
Silicon 0.1 to 2.5%
Manganese 2.5% max
15 Nickel 30 to 45%
Chromium 19 to 22%
Molybdenum 3.0% max.
Niobium 2.0% max.
Hafnium 0.01 to 4.5%
20 Titanium 0.5% max.
Zirconium 0.5% max.
Cobalt 2.0% max.
Tungsten 1.0% max.
Aluminium 0 - 15.0%
25 Nitrogen 0.001 - 0.5%
Oxygen 0.001 - 0.7%
balance iron and incidental impurities.

9. An alloy according to any one of claims 1, 2, 3, 5,
30 or 7, having a carbon content of from 0.3 to 0.5% by weight.

10. An alloy according to claim 1 or 2, having a carbon
content of from 0.03 to 0.2% by weight.

35

31

11. An alloy according to claim 1, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.01 to 3.0%.
- 5 12. An alloy according to claim 11, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.1% to 1.0%.
- 10 13. An alloy according to claim 11 or 12, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.2 to 0.5%.
- 15 14. An alloy according to any one of the preceding claims, in which the amount of carbon in the alloy, by weight, is from 0.03 to 0.2% and the amount of hafnium in the alloy, by weight, is from 1 to 4.5%.
- 20 15. An alloy according to any one of claims 1 and 4 to 8, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 10% and the amount of hafnium by weight is from 0.01% to 4.5%.
- 25 16. An alloy according to claim 15, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 6% and the amount of hafnium by weight is from 0.1% to 1.0%.
- 30 17. An alloy according to claim 15 or 16, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 4.5% and the amount of hafnium by weight is from 0.2% to 0.5%.
- 35

18. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 50
5 microns to 0.25 microns, or less.

19. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles
10 having an average particle size of from 5 microns to 0.25 microns, or less.

20. An alloy according to any one of the preceding claims, having any one of the following
15 compositions, by weight:

| | | |
|----|------------|----------|
| | Carbon | 0.45% |
| | Silicon | 1.3% |
| | Manganese | 0.9% |
| 20 | Nickel | 33.8% |
| | Chromium | 25.7% |
| | Molybdenum | 0.03% |
| | Niobium | 0.85% |
| | Hafnium | 0.25% |
| 25 | Titanium | 0.1% |
| | Zirconium | 0.01% |
| | Cobalt | 0.04% |
| | Tungsten | 0.01% |
| | Nitrogen | 0.1% |
| 30 | Iron | balance. |

| | | |
|----|-----------|-------|
| | Carbon | 0.07% |
| | Silicon | 1.0% |
| | Manganese | 0.98% |
| 35 | Nickel | 32.5% |

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33

| | | |
|----|------------|----------|
| | Chromium | 25.8% |
| | Molybdenum | 0.20% |
| | Niobium | 0.04% |
| | Hafnium | 1.1% |
| 5 | Titanium | 0.12% |
| | Zirconium | 0.01% |
| | Cobalt | 0.04% |
| | Tungsten | 0.08% |
| | Nitrogen | 0.1% |
| 10 | Iron | balance. |

| | | |
|----|------------|---------|
| | Carbon | 0.34% |
| 15 | Silicon | 1.68% |
| | Manganese | 1.10% |
| | Nickel | 32.0% |
| | Chromium | 21.3% |
| | Molybdenum | 0.01% |
| 20 | Niobium | 0.80% |
| | Hafnium | 0.25% |
| | Titanium | 0.12% |
| | Zirconium | 0.01% |
| | Aluminium | 3.28% |
| 25 | Cobalt | 0.04% |
| | Tungsten | 0.01% |
| | Iron | balance |

| | | |
|----|------------|-------|
| | Carbon | 0.42% |
| 30 | Silicon | 1.79% |
| | Manganese | 1.17% |
| | Nickel | 33.2% |
| | Chromium | 23.3% |
| | Molybdenum | 0.02% |
| 35 | Niobium | 0.77% |

| | | |
|---|-----------|---------|
| | Hafnium | 0.24% |
| | Titanium | 0.10% |
| | Zirconium | 0.01% |
| | Aluminium | 1.64% |
| 5 | Cobalt | 0.04% |
| | Tungsten | 0.08% |
| | Iron | balance |

10 21. An oxide dispersion strengthened nickel-chromium-iron alloy which comprises up to about 5% by weight of hafnium, with at least part of the hafnium being present as finely divided oxidised particles.

15 22. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that at least part of the hafnium is converted to oxide in the melt.

20 23. A method according to claim 22, in which the alloy is an alloy as claimed in any one of claims 1 to 21.

25 24. A method according to claim 22 or 24, wherein the hafnium particles have a particle size of less than 50 microns.

30 25. A method according to any one of claims 22 to 24, in which the amount of hafnium added to the melt is from 0.01 to 3.0% by weight.

35 26. A method according to any one of claims 22 to 25, wherein the hafnium particles are added to the melt shortly before pouring the molten alloy into a mould.

27. A method according to claim 26, in which the hafnium particles are added to the molten alloy in a ladle.
- 5 28. A method according to any of claims 22 to 27, in which the hafnium is electrolytic hafnium.
29. A method according to any one of claims 22 to 28, wherein the level of oxygen in the melt is varied by
10 additions of one or more of niobium, titanium and zirconium.
30. A method according to claim 29, in which the titanium is added in the form of TiFe after the
15 hafnium addition.
31. A method according to any of claims 22 to 30, in which the melt temperature is in the range of from 1500°C to 1700°C.
20
32. A method of manufacturing a corrosion resistant nickel-chromium-iron which comprises adding sequentially finely divided hafnium particles and aluminium to a melt of the alloy before pouring.
25
33. A method according to claim 32, wherein the aluminium is added to the melt immediately before pouring the molten alloy into a mould.
- 30 34. A method according to any one of claims 22 to 33, in which the alloy is formed into a tube by rotational moulding.
- 35 35. A method of manufacturing a nickel-chromium-iron alloy, which comprises adding finely divided hafnium

36

particles to the melt before pouring.

- 5 36. A creep resistant alloy tube according to claim 42, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to about 5% of hafnium.
- 10 37. A tube formed from an alloy according to any one of claims 1 to 21 by rotational moulding.
- 15 38. A nickel-chromium-iron alloy having a structure and composition substantially as described and illustrated in any one of Figures 1 to 4 of the accompanying Drawings, wherein the tables represent percentages by weight of the alloy constituents.
- 20 39. A nickel-chromium-iron alloy having a structure substantially as described and illustrated in Figures 5 or 6 of the accompanying Drawings.
- 25 40. A corrosion resistant tube, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to 15% of aluminium and up to about 5% of hafnium.
41. An alloy according to any one of claims 1 to 21, 38 and 35 produced by a method according to any one of claims 22 to 35.